PROPERTIES OF POLY(VINYL BUTYRAL)/TiO$_2$ NANOCOMPOSITES FORMED BY SOL-GEL PROCESS

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Introduction

Progress of sol-gel process, which synthesizes ceramics at low temperature, has made it possible to prepare novel organic/inorganic nanocomposites (Wen et al., 1996). They have the possibility to become new materials having both advantages of the organic materials such as the lightweight, flexibility, and good moldability, and of the inorganic materials such as the high strength, heat-stable, and chemical resistance. Poly(vinyl butyral) (PVB) is sturdy and flexible. Especially, it is known for its high impact strength at low temperatures. Furthermore, PVB has excellent adhesive properties with many materials such as glass, metal, plastics and wood. Thus, PVB is widely used as a paint, an adhesive agent, a printing paste and a film sandwiched in a safety glass for automobiles (Blomstrom 1990). The author considered that a nanocomposite of PVB and glass could be expected to change and its functions to develop. Fu et al. prepared silica/PVB hybrid material and used as a support of ternary europium complexes and phenanthroline (Fu et al. 1999). But, the properties of the hybrid have not been reported. We will report the properties of PVB/titanium oxide (TiO$_2$) nanocomposites prepared by the sol-gel process.

Experimental

Materials

Poly (vinyl butyral) (PVB: degree of polymerization = 700) was obtained from Wako Pure Chemical Ind., Ltd. and used without any purification.

Titanium tetraisopropoxide (0.1mol, Wako Pure Chemical Ind., Ltd.) was diluted by ethanol (100ml). Hydrochloric acid (HCl) (2N, 2.7ml) was poured and stirred into this solution, resulting in a transparent TiO$_2$ sol (Yoko et al. 1987). A fixed amount of TiO$_2$ sol was added to PVB 5 wt% ethanol solution. This mixed solution was aged at room temperature in a sealed dish for 48 h, and the transparent PVB/TiO$_2$ nanocomposite films (thickness, 50µm) were obtained by drying wet gel at 40°C in air and further in vacuo. The nanocomposites obtained will be designated by an abbreviation; for example, the final nanocomposite containing TiO$_2$ of 10 wt% will be called T-10.

Results and Discussion

All samples prepared were colorless and transparent. Table 1 shows the mechanical properties obtained from the stress-strain (s-s) curves for each sample. The Young’s modulus of T-15 is about 2.4 times higher than that of pure PVB. In the case of poly(vinyl alcohol)(PVA)/silica system (Nakane et al. 1999), the Young’s modulus increases from 31.8 for pure PVA to 45.2 MPa for the nanocomposite of silica 15 wt%. The increase is 1.4 times. Thus it is considered that the TiO$_2$ particles disperse effectively in polymer matrix. The yield stress also increases but the elongation at break decreases with increasing TiO$_2$ content.

Table 1 Magnetic Mechanical properties of PVB/TiO$_2$

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young’s Modulus (GPa)</th>
<th>Yield Stress (GPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVB</td>
<td>0.95</td>
<td>13.7</td>
<td>4.9</td>
</tr>
<tr>
<td>T-5</td>
<td>1.44</td>
<td>29.6</td>
<td>3.9</td>
</tr>
<tr>
<td>T-10</td>
<td>1.91</td>
<td>39.5</td>
<td>3.5</td>
</tr>
<tr>
<td>T-15</td>
<td>2.25</td>
<td>-</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Pure PVB and T-5 showed the typical s-s curve which has the yield point and the strain after the point. On the other hand, an s-s curve in which the break occurred immediately after the yield point was observed for T-10, and the breaking occurred before the yield point for T-15. The change of the fracture mechanisms, from the ductile fracture to the brittle fracture, was observed at around 10 wt% of TiO$_2$ content in the PVB matrix.

Fig.1 shows the DMA curves of the nanocomposites. The peak of the tanδ become lower and shifted to a high
temperature gradually with increasing the TiO$_2$ content [corresponding to the glass transition temperature ($T_g$) of PVB] (The $T_g$ is about 75°C for pure PVB, and the $T_g$ for T-15 is 96 °C). In addition, as the TiO$_2$ content is increased, the decreases of the storage modulus at around the $T_g$ become gentle, and high moduli are maintained at high temperature ranges (ex. the order of 10$^8$ Pa for T-15). The measurement could not be carried out for pure PVB at a temperature higher than 110°C due to the softening, but it was possible for the nanocomposites up to at least 150 °C. Thus the nanocomposites have higher thermal resistance than pure PVB. It is considered that TiO$_2$ is dispersed homogeneously in PVB, and the thermal motion of the PVB segment is prevented by the interaction between them.

Fig. 1 Thermomechanical spectra of PVB/TiO$_2$ nanocomposites.

Fig. 2 shows the result of abrasion test. The ordinate means the number of friction cycle when the sample was broken down. The mixing of TiO$_2$ improves the abrasion resistance of PVB. This result may be ascribed to the decrease of surface frictional resistance and the increase of hardness associated with increase the TiO$_2$ content in the nanocomposites.

The TPNR-CNTs/Fe$_3$O$_4$ composites were successfully prepared by a combined ball-milling and melt-blending technique. The XRD results reveal that the acid treatment of CNTs does not influence the structure of TPNR and Fe$_3$O$_4$ nanoparticles, while the acid-treated CNTs alter the magnetic property of the composites. This can be attributed to the disentanglements of CNTs by acid treatment which results in better magnetic property.

Fig. 2 Effect of TiO$_2$ content on abrasion resistant for PVB/TiO$_2$ nanocomposites.

**Conclusion**

The properties of PVB/TiO$_2$ nanocomposite films were investigated. By the mixing TiO$_2$ with PVB matrix, the nanocomposites became stiff and brittle, and the thermal and abrasion resistance were improved. We consider that the PVB/TiO$_2$ nanocomposites can be used as not only a film but also a coating material with excellent durability.

**References**